

R. Deformation Processes for Next-Generation Ceramics

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Objectives

- Assess the plastic deformation behavior in nanocrystalline oxide ceramics and its applicability to fabrication of complex shapes.
- Characterize the ability to deform nanocrystalline ceramics at temperatures well below 1000°C through control of microstructure and external parameters (e.g., electric fields, environment).
- Characterize thermal and mechanical properties to assess the influence of nanocrystalline microstructures for gaining improved performance for wear and other components.

Approach

- Collaborate with members of the Pennsylvania State University task on Synthesis of Nanocrystalline Ceramics to develop advanced colloidal technology-based processing to fabricate monolithic bodies and sintering technology to fabricate dense monolithic nanocrystalline bodies (i.e., grain sizes <100 nm).
- Conduct both compressive creep and plastic deformation studies as a function of temperature, environment, and applied electric fields on nanocrystalline oxides with grain sizes of <100 nm.

Accomplishments

- Established a novel pressureless sintering method to fabricate dense monolithic zirconia bodies with selected grain sizes in the range of 20 to 90 nm.
- Developed data on the deformation of dense zirconia ceramics with a grain size of 350 nm to serve as a baseline for comparison of future observations. Initial observations have been obtained on the enhancement of deformation of this dense zirconia ceramic with sub-micron-sized grains from applied electric fields through collaboration with North Carolina State University researchers.

Future Direction

- Exploit the ability to sinter monolithic nanocrystalline oxides to full density to characterize the enhanced plastic deformation below 1000°C in zirconia ceramics having grain sizes below 100 nm. The goal is to explore the minimum temperature at which permanent deformation can still be achieved.
- Evaluate conditions required for optimizing deformation-shape forming.

- Examine room temperature fracture and wear properties to seek approaches for developing ceramics with greater wear resistance.
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Introduction

In addition to lower specific weight, ceramics have a number of attractive properties for application as components in various heavy vehicle systems. However, many heavy vehicle components require ceramics with complex shape as well as function. Furthermore, the demanding service conditions necessitate improved mechanical reliability together with fracture and/or wear resistance. Underlying the performance and use of ceramics is their tendency to fail in a brittle fashion except at temperatures generally well above 1000°C. Complex-shape-forming processes for ceramics are relegated to approaches based on powder processing as a result of the excessive temperatures for hot forming. On the other hand, metallic alloys can be hot-worked at temperatures below 1000°C not only to form the desired shape but also to enhance their properties. The ductility (>20% plastic strain) of metallic alloys at temperatures below 500°C is the source of their 10- to 100-fold greater fracture toughness compared with ceramics.

In ceramic systems, processing to tailor microstructures needs to be combined with novel concepts that offer the potential to enhance deformation. One such concept that has been of considerable interest is superplastic deformation of ceramics with sub-micron-size grains at temperatures above 1000°C.¹ Recent studies suggest that reducing the microstructure to achieve grain sizes of <100 nanometers could lead to permanent/plastic deformation in ceramics at quite modest temperatures.^{2,3} Indeed, classical deformation behavior suggests significant decreases in yield stresses at a fixed temperature or decreases in temperature at which deformation can be induced via the reduction in grain size.⁴ Typically, temperature, strain rate or stress, and grain size are the parameters to alter the deformation or creep rates in single-phase oxides. Recent studies have shown that the application of electric fields can reduce the yield stress or increase the creep rates of ceramic systems.⁵ To date, this has not been exploited to determine the effects on the deformation of nanocrystalline oxides. The present study seeks to examine the influence of true nanocrystalline microstructures on

the mechanical properties of ceramics, as well as approaches to economically fabricate nanocrystalline ceramic monoliths.

Approach

This project involves two major thrusts. The first is a collaborative effort in the processing and sintering of nanocrystalline ceramics with researchers in the Synthesis of Nanocrystalline Ceramics task at Pennsylvania State University. The goal is to develop the technology to form “green” (unfired) bodies of nanocrystalline particles with densities well in excess of 50% of the theoretical density, which will allow us to devise pressureless sintering profiles to produce dense monolithic bodies with grain sizes of <100 nm (see ref. 6 for a review of processing of nanocrystalline ceramics). This is aimed at finding approaches to produce sizeable monolithic bodies for subsequent evaluation.

The second thrust focuses on the mechanical and wear behavior of nanocrystalline ceramics and the influence of external parameters [e.g., stressing rate, temperature, environment (e.g., air, vacuum), and electric fields] on the plastic deformation behavior.

Synthesis, Evolution, and Stability of Nanostructures in Bulk Materials

Outstanding challenges in particle processing to form bulk, dense nanograin-size materials include the dispersion of the nanosize particles and control of gas evolution from the very-high-surface-area compacts during sintering. Typically, nanometer-size particulates suffer from a high degree of agglomeration, which results in poor particle packing (green densities < 40% of theoretical); this inhibits sintering and promotes undesirable grain growth. Two routes to obtaining well-dispersed powders include comminution and colloidal processing.^{7,8} By optimizing colloidal processing approaches, it should be possible to produce green bodies with densities of more than 60% of the theoretical by control of interparticle forces. This control is achieved through appropriate chemical additives to suspensions of nanoparticulates, combined with filter pressing or pressure casting of the high-solids-

content slurries. By controlling the packing of nanoparticles, one should be able to control the porosity to achieve the narrow size distribution necessary, which then will enhance densification.

Densification of nanocrystalline ceramics has typically involved the use of applied pressure to achieve dense samples with sub-100-nm grain size.⁹ In those few cases where pressureless sintering has been employed successfully, long hold times at the sintering temperatures were required to achieve densities $\geq 95\%$ of theoretical, which allow undesired grain growth to proceed.¹⁰ Heating to a temperature sufficient to achieve densities of $\geq 75\%$ of theoretical, and then rapidly lowering the temperature to obtain sufficient boundary diffusion to remove pores trapped on boundaries while minimizing grain growth, has been only partially successful. Long hold times at the lower temperature were still required.¹¹ Here we seek to optimize the processing of the green bodies and use modified sintering cycles to achieve dense oxides with sub-100-nm grain sizes.

Deformation Behavior in Nanostructured Materials

To evaluate the influence of nanocrystalline microstructures, baseline deformation data will be established through studies of high-purity, dense zirconia ceramics with sub-micron-size grains. These studies will then be extended to ceramics with <100 nm grain size. This will include

- nanostructured ceramics, to explore for the softening effects observed in nanocrystalline metals by evaluating both (1) the creep response over a range of temperatures and applied stresses and (2) the yield stress as a function of strain rate and temperature
- the influence of external factors (e.g., electric fields) that have been shown to enhance deformation processes in ceramics with micrometer grain sizes

Modeling studies will be conducted to describe the deformation behavior and to address such phenomena as space charge/solute segregation coupled with electric field effects. Additionally, the fracture, hardness, and wear response of nanocrystalline oxides will be evaluated to assess their application in wear components.

Results

Sintering

Advanced colloidal processing in the task on Synthesis of Nanocrystalline Ceramics has provided monolithic green bodies of both yttria-doped and undoped zirconias with densities from 55 to 68 % of theoretical and an average particulate size of 15 nm. Advanced sintering cycles now allow the production of dense monolithic zirconias with grain sizes well below 100 nm (Figure 1). As noted, sintering in a vacuum promotes densification at lower temperatures than sintering in air. At this point, we assume this is due to lower capillary pressure within pores and faster removal of any residual organics or moisture used in the colloidal processing.

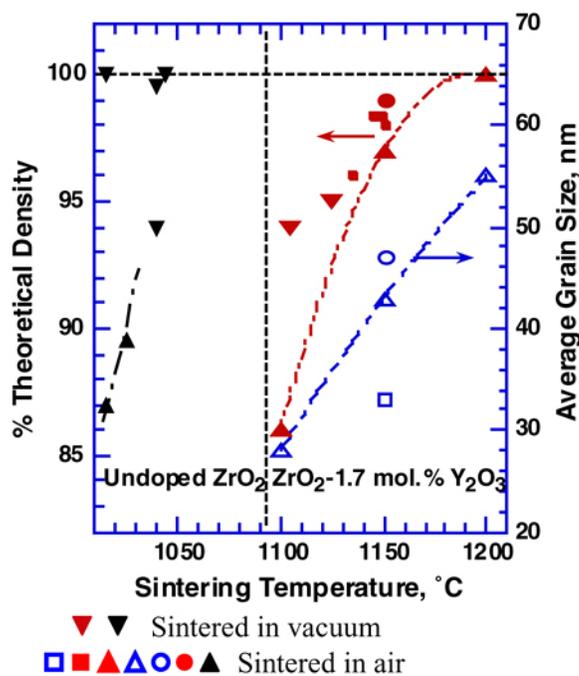


Figure 1. Pressureless sintering of colloidally processed zirconias yields dense ceramics with grain sizes < 100 nm (density—closed symbols; open symbols—grain size).

Based on the data shown in Figure 1, it is obvious that the addition of yttria inhibits the densification of nanocrystalline zirconia. Recent work indicates that space charge effects due to yttrium segregation may inhibit Zr^{+4} lattice diffusion,^{12,13} which would explain the lower-than-expected creep deformation observed in yttria-doped zirconia with grains of sub-100-nm size (Figure 2).¹⁴ While grain boundary diffusion is a critical factor in the removal of pores

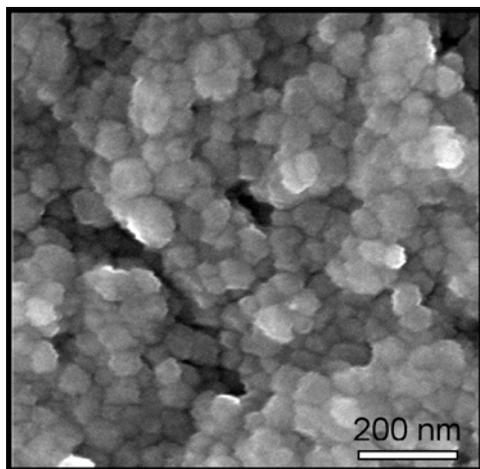


Figure 2. Microstructure of ZrO₂—1.7 mol % Y₂O₃ ceramic sintered in air at 1150°C.

during the densification of nanoparticulate bodies, lattice diffusion might be a limiting parameter in sintering.

Deformation Studies

In the first year of this project, a fully dense, hot-isostatically-pressed zirconia—2 mol % yttria ceramic with a grain size of ~ 350 nanometers (Figure 3)—was selected for studies of compressive deformation. These include compressive creep and constant strain rate deformation studies conducted in air at temperatures above 1000°C to obtain measurable deformation. These results will serve as a baseline for assessing the effectiveness of increasing the plasticity by producing microstructures of sub-100-nm grain size. In addition, data on the tetragonal zirconia ceramic with 350-nm grain size can be used to correlate with data in the literature on zirconias with sub-micron grain size.

The creep behavior illustrates the creep rate dependence on applied stress above 1100°C with stress exponents of 1.7 to 1.9, while at 1100°C the stress exponent is ~ 0.6 (Figure 4a). The activation energy ranges from 625 to 645 kJ/mol with a discontinuity at 1100°C with a stress of 30 MPa (Figure 4b). The stress exponent and the activation energy values are similar to those reported in the literature for high-purity zirconias with grains of sub-micron size;¹⁴ however, the test temperatures were typically greater than 1200°C. The extent of permanent deformation was limited by the displacement range of the contact extensometers, which require repositioning for displacements of 150 to 200 microns, or by the length

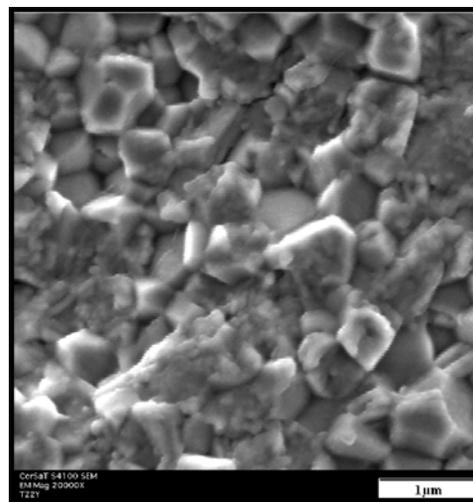


Figure 3. Fracture surface microstructure of 350 nm grain sized tetragonal zirconia—2 mol. % yttria ceramic used to establish baseline data on deformation behavior.

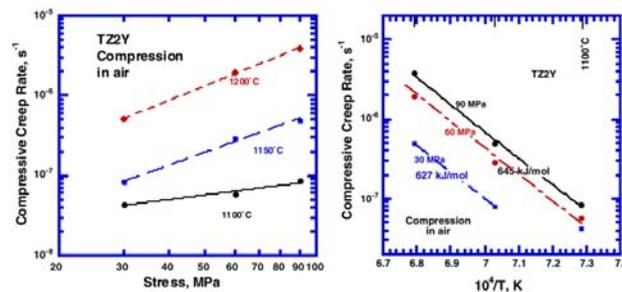


Figure 4. Applied stress (a) and temperature (b) dependence of the compressive creep rates of submicron grain sized ZrO₂—2 mol% Y₂O₃ in air.

of the test in the case of those conducted at 1100°C. However, permanent strains of ≥ 2 % were obtained based on measurements prior to and after testing.

Initial assessments of the compressive yield stresses of this sub-micron-grain-size zirconia were obtained in air. Data at 1300°C reveal a typical decrease in the yield stress as the stress rate is reduced (Figure 5a). At the same time, the yield stress increased significantly when the temperature was reduced to 1200°C for comparable stress rates (Figure 5b). Thus permanent strains under dynamic loading in air were limited to <2 %. On the other hand, observations reveal that extensive plastic strain (~ 45%) could be achieved at 1200°C with the application of a dc field of 1 kV/cm in this sub-micron-grain-size zirconia. In view of the recent observations of plasticity in nanocrystalline zirconia

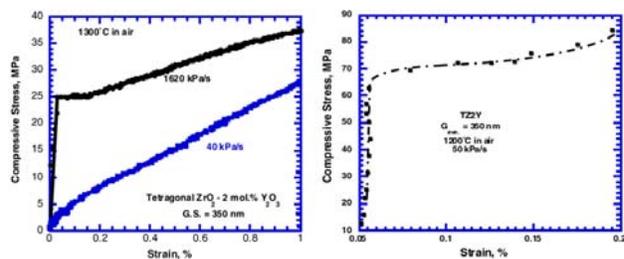


Figure 5. Compressive yielding of 350-nm-grain sized ZrO_2 ; 2 mol % Y_2O_3 exhibits typical decrease in yield stress due to reduction in stressing rate at 1300°C in air (a) and an increase with decrease in test temperature (b).

ceramics at 1000°C,³ there would appear to be significant potential for enhanced plasticity in nanocrystalline zirconias. The demonstrated ability in the current task to fabricate dense monolithic nanocrystalline zirconia ceramics will now allow us to evaluate the plastic deformation behavior of doped and undoped zirconia ceramics over a range of grain sizes (i.e., 30 to 100 nm).

Conclusions

Advances in the processing of monolithic nanoparticulate zirconia bodies with green densities in excess of 55% of theoretical, through our collaboration with the task on Synthesis of Nanocrystalline Ceramics, now allow us to fabricate dense monolithic bodies of both yttrium-doped and undoped zirconias with grain sizes well below 100 nm by pressureless sintering. This is a substantial innovation and provides the critical path forward to assessing the plastic deformation behavior of nanocrystalline oxides, as well as other properties (e.g., wear, strength) that would prove advantageous for improvements in heavy vehicle component fabrication and performance.

Baseline data on the deformation response of zirconia ceramics are being established using a fully dense 350- μ m grain-size tetragonal zirconia containing 2 mol % yttria. Results show that this ceramic can be plastically deformed in compression to permanent strains in excess of 2% at stresses below 100 MPa and temperatures of 1200 to 1300°C in air. Current work is focusing on the preparation of compression samples with sub-100 nm grain size to begin evaluating the deformation behavior of nanocrystalline (<100 nm) ceramics.

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Publications

C. H. Hsueh and P. F. Becher, "Effects of Dopant Segregation on Lattice-Diffusional Creep of Nanocrystalline Ceramics," *Phys. Rev. B*, accepted for publication.